Electron microscopy study of the deactivation of nickel based catalysts for bio oil hydrodeoxygenation

Gardini, Diego; Mortensen, Peter Mølgaard; Carvalho, Hudson W. P.; Damsgaard, Christian Danvad; Grunwalst, Jan-Dierk; Jensen, Peter Arendt; Jensen, Anker Degn; Wagner, Jakob Birkedal

Published in:
Microscopy and Microanalysis

Link to article, DOI:
10.1017/S1431927614004012

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

doi:10.1017/S1431927614004012
Microsc. Microanal. 20 (Suppl 3), 2014

Electron Microscopy Study of the Deactivation of Nickel Based Catalysts for Bio Oil Hydrodeoxygenation

Diego Gardini[1], Peter M. Mortensen[2], Hudson W. P. Carvalho[3], Christian D. Damsgaard[1,4], Jan-Dierk Grunwaldt[3], Peter A. Jensen[2], Anker D. Jensen[2] and Jakob B. Wagner[1]

[1.] Technical University of Denmark, Center for Electron Nanoscopy, DK-2800 Kgs. Lyngby, Denmark.
[2.] Technical University of Denmark, Department of Chemical and Biochemical Engineering, DK-2800 Kgs.Lyngby, Denmark.
[3.] Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, 76131 Karlsruhe, Germany.
[4.] Technical University of Denmark, Center for Individual Nanoparticle Functionality, Department of Physics, DK-2800 Kgs. Lyngby, Denmark.

Hydrodeoxygenation (HDO) is proposed as an efficient way to remove oxygen in bio-oil, improving its quality as a more sustainable alternative to conventional fuels in terms of CO_2 neutrality and relative short production cycle [1].
Ni and Ni-MoS_2 nanoparticles supported on ZrO_2 show potential as high-pressure (100 bar) catalysts for purification of bio-oil by HDO. However, the catalysts deactivate in presence of sulfur, chlorine and potassium species, which are all naturally occurring in real bio-oil.
The deactivation mechanisms of the Ni/ZrO_2 have been investigated through scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Catalytic testing has been performed using guaiacol in 1-octanol acting as a model compound for bio-oil.

Addition of sulphur (0.3 vol% octanethiol) in the feed resulted in permanent deactivation of the catalyst by formation of a catalytically inactive Ni-S phase, as suggested by the very similar spatial distribution of nickel and sulphur signals in STEM-EDX elemental maps (Figure 1) and confirmed by XRD and X-ray absorption spectroscopy (XAS) techniques.
Deactivation by chlorine (0.3 vol% chlorooctane) co-feeding was found to be reversible, as the catalyst could regain close to its initial deoxygenation activity upon restoration of a clean feed. SEM-EDX investigations excluded the presence of chlorine species; however, XRD analysis revealed sintering of nickel nanoparticles (Figure 2).
Impregnating KCl and KNO3 on two different batches of catalysts decreased permanently their deoxygenation activity, suggesting the adsorption of potassium at low coordinated nickel sites [2]. The high mobility of potassium under the electron beam [3] prevented the spatial distribution study of this element through STEM-EDX. Moreover, nickel sintering was observed in the KCl poisoned sample and was ascribed once again to the formation of mobile Ni-Cl species upon reaction of HCl with surface oxides [4].

Furthermore, environmental transmission electron microscopy (ETEM) has been used in order to investigate the oxidation of Ni-MoS_2/ZrO_2 catalyst active phase as a function of different HDO reaction conditions and using methanol as a model molecule for bio-oil.

References:

[1] P. M. Mortensen *et al,* Appl. Catal. A: Gen. **407** (2011) p. 1-19.
[2] H. S. Bengaard *et al,* J. Catal. **209** (2002), p. 365-384.
[2] S. Hodson and J. Marshall, J. Microsc. **93** (1971), p. 49-53.
[3] Y. Ohtsuka, J. Mol. Cat. **54** (1989), p. 225-235.

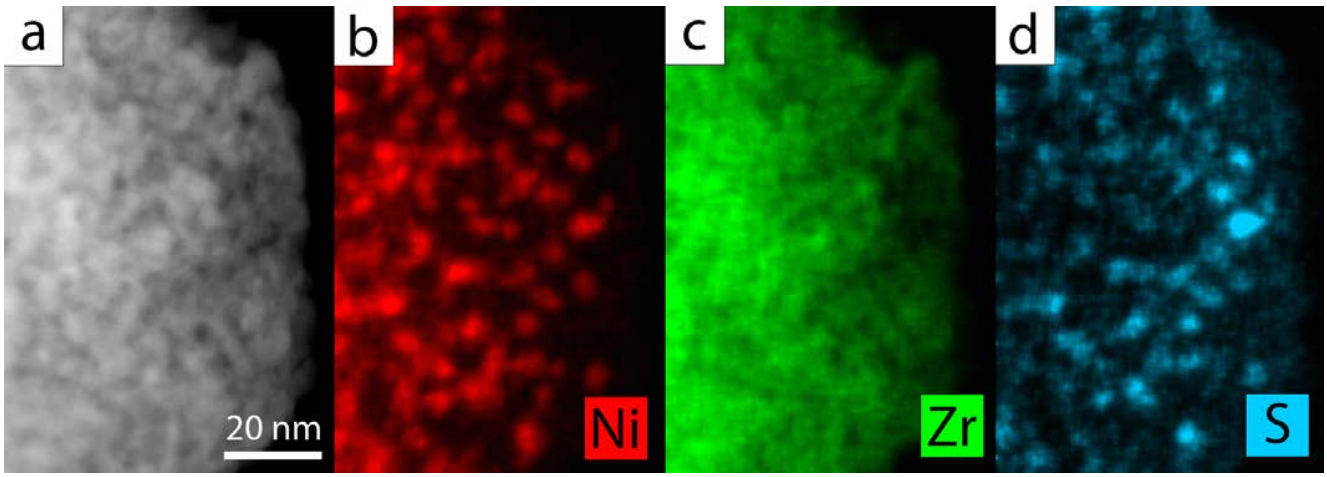

Figure 1. (a) STEM-HAADF micrograph of a portion of a sulfur poisoned Ni/ZrO_2 catalyst with (b) nickel, (c) zirconium and (d) sulfur EDX elemental distributions.

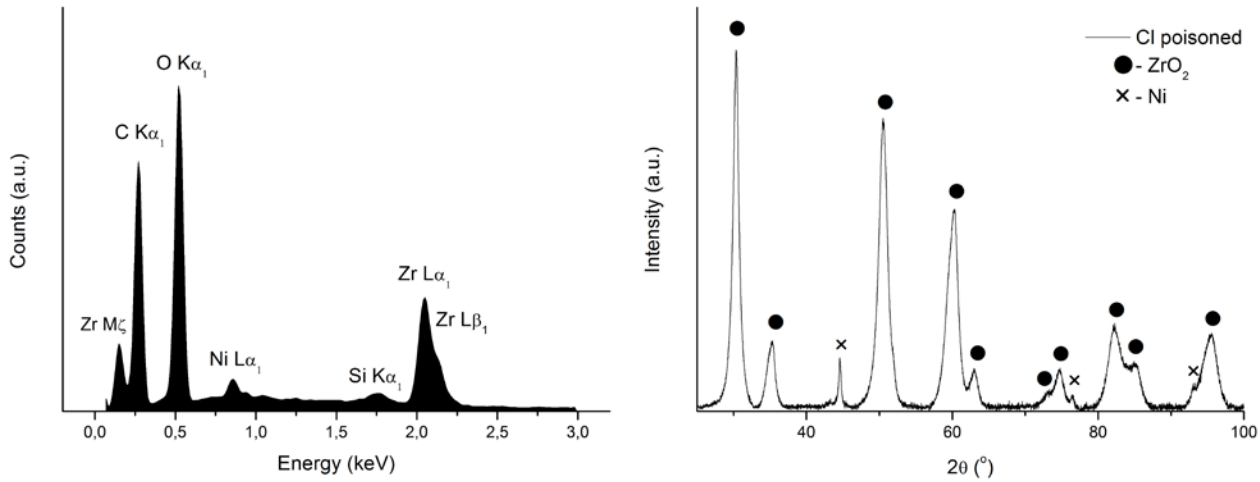

Figure 2. (Left) SEM-EDX spectrum of the chlorine poisoned catalyst and (right) X-ray diffraction pattern of the same catalyst.